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Pigments and preparation layers characterization of a Saint John the Evangelist painting using X-ray Fluorescence technique and Raman spectroscopy

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1. Introduction

In last decades, many scientific techniques have been employed in studies of cultural heritage and works of art. The identification of the pigments used in paintings is important to characterize the artist's working methods, to assist in conservation processes, since it can help to distinguish the original compounds of a painting from restored or retouched ones and for preservation; depending on their nature, pigments may be sensible to light, humidity, atmospheric pollutant or heat, which may require specific storage or display condition [1].

Many works of art and historical artifacts have a great historical/cultural value, therefore, whenever possible, non-destructive analytical techniques should be used. The use of only one technique may not always be sufficient to characterize a historical artifact, usually due to its manufacturing process, hence different techniques and methods have been developed and successfully used for scientific investigation of cultural heritage, such as X-ray fluorescence (XRF) [2,3], Raman spectroscopy [4] and Fourier transform infrared (FTIR) [5].

In this work, the pigments and the ground layers of a Saint John the Evangelist painting were characterized by X-ray fluorescence (XRF) and micro-Raman spectroscopy techniques for the propose of assisting in dating of the painting. The painting was purchased by a collector at an auction as a 19th century work of unknown authorship.

2. Methodology

The X-ray Fluorescence spectra were obtained using the portable Energy Dispersive X-ray Fluorescence (ED-XRF) equipment developed in our own laboratory [3]. The portable ED-XRF system used has a low power X-ray tube (Amptek) with a silver anode [Ag] and an SDD detector (Amptek) with an energy resolution of 122 eV @5.9 keV. In addition, the system has laser alignment. Figure 1 shows the St. John the Evangelist painting and the points analyzed. Measurement setup was as follows: tube voltage 40 kV, current 50 µA, acquisition time 60 s and no filter.

A fragment sample of the background's black pigment was collected and analyzed by micro-Raman spectroscopy. Micro-Raman spectroscopy measurements were performed using a Thermo Scientific – DXR2 Raman microscope equipment. The sample was excited by the 785 nm adjusted laser source with power of 4 mW, focused on the sample by means of 100x objective. The spectra were collected in the 100-2000 cm^{-1}

range, with acquisition time of 3s and 10 accumulations were performed.

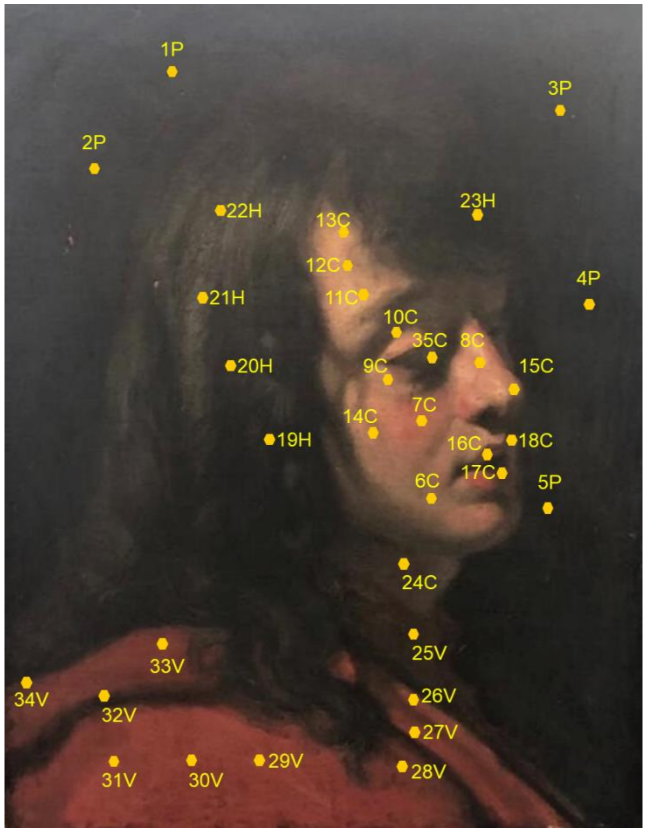

Figure 1: Points analyzed by XRF in the painting of Saint John the Evangelist.

3. Results and Discussion

The XRF analysis of the black pigment present in the background and in the eye showed the presence of the elements: phosphorus (P), calcium (Ca), manganese (Mn), iron (Fe), copper (Cu) and lead (Pb).

The Pb element was identified in all analyzed points, suggesting that this work was painted over a preparation layer made of Lead White [$PbSO_4.PbO$]. The variation of Pb-M lines in all spectra supports this hypothesis. Lead White pigment was used from antiquity to the 19th century, after which it was replaced by less toxic pigments such as Titanium White and Zinc White [6].

The presence of the elements P and Ca found in the analysis of the black pigment suggests that this pigment may be the Carbon Black/Bone black [$Ca_5(OH)(PO_4)_3$], which is a pigment used since pre- history, and is obtained by the carbonization of animal bones, containing about 10 to 20% of carbon. The remainder of the material consists of hydroxyapatite [$Ca_5(OH)(PO_4)_3$] and calcium sulfate [7]. In the Raman spectroscopy analysis of the black pigment, the wavenumber bands detected were 1582 and 1320 cm^{-1}. These bands correspond to the Carbon Black pigment, corroborating the results of XRF.

Furthermore, the Mn and Fe present in the black pigments could suggest a mixture with an earth pigment, as Ocher [Fe_2O_3].

In St. John the Evangelist's hair, there is a shaded hue and an illuminated hue. The elements detected in the black pigment used in the hair were: phosphorus (P), calcium (Ca), manganese (Mn), iron (Fe), copper (Cu) and lead (Pb).

In the illuminated hue of the hair, it wasn’t possible to detect the P element. Furthermore, both the Pb intensities and the ratios between the Pb-M and Pb-L lines increased, suggesting that a layer of Lead White was applied over the black pigment to produce this light effect.

In the XRF analysis of the pigments used in the carnation, it was possible to detect the elements: calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), mercury (Hg) and lead (Pb). It can be highlighted the elements Fe, Hg and Pb as key elements of the pigments Ocher [Fe_2O_3], Vermilion/Vermilion [HgS] and Lead White [$PbSO_4$.PbO] respectively.

Vermilion is a pigment of mineral and synthetic origin widely used from antiquity to the 19th century [8].

The XRF analysis from the red pigment of the Saint John the Evangelist's tunic, show the presence of the elements: calcium (Ca), iron (Fe), copper (Cu), mercury (Hg) and lead (Pb).

Pb and Hg indicate the presence of Lead White and Vermilion pigments.

In the St. John the Evangelist's tunic, it is also possible to notice two shades of red. A darker one and a lighter one.

In the red hues' XRF analysis was possible to notice that the Cu intensity was higher in the darker red hue. Cu is usually found in green or blue pigments such as Malachite [$Cu_2(OH)2CO_3$], Verdegris [$Cu(CH_3COO)_2$] and Azurite [$2CuCO_3 \cdot Cu(OH)_2$]. However, Cu can also be found in the pigment Tenorite [CuO], which is a mineral origin pigment, and can often be found in pigments of earth origin, such as Ocher.

The Red Ocher pigment is used from prehistory to the present day [8].

Through the XRF technique, it was also possible to detect the elements S, Ca, Mn, Hg and Pb, present on the back of the canvas. The Hg-M and Pb-M lines were not detected. On the other hand, a large concentration of these elements was identified in the pigments of the painting, it is possible to conclude that these elements are not characteristic elements of the canvas material, but rather of the pigments. Ca and S elements suggest the presence of gypsum ($CaSO_4$).

Table 1 presents all the elements found in the analyzed regions and the suggested pigments for these regions. The underlined elements are the characteristic elements of each pigment.

Table 1: Elements detected in the analyzed regions and the suggested pigments for these regions.

Analyzed region	**Elements**	**Suggested pigments**
Carnation	Ca, Mn, Fe, Cu, Hg and Pb	Ocher [Fe_2O_3], Lead White [$PbSO_4$.PbO] and Vermilion [HgS]
Hair (black)	P, Ca, Mn, Fe, Cu and Pb	Carbon Black [Ca5(OH)(PO4)3] and Ocher [Fe_2O_3]
Background and Eyes (black)	P, Ca, Mn, Fe, Cu and Pb	Carbon Black [Ca5(OH)(PO4)3] and Ocher [Fe_2O_3]
Tunic (red)	Ca, Fe, Cu, Hg and Pb	Vermilion [HgS], Ocher [Fe_2O_3] and Lead White [$PbSO_4$.PbO]

4. Conclusions

According to the results obtained in the XRF analysis, it was possible to characterize the pigments used in the Saint John the Evangelist painting as Lead White, Vermilion, Carbon Black and Ocher. No repainting areas and modern pigments were identified that could suggest any kind of intervention.

The presence of Lead White pigment in the preparation layers and in the lighting of other pigments suggests that the work predates the 19th century. The Vermilion pigment, on the other hand, had been in use from antiquity to the 19th century, suggesting that this work had been made until the end of the 19th century.

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References

[1] R. Molari et al., “Non-destructive portable X-ray fluorescence analysis of the Portrait of a Young Man with a Golden Chain (c. 1635) by Rembrandt and/or atelier”, *Applied Radiation and Isotopes*. vol. 165 (2020).

[2] R. Cesareo et al., “Pre-Columbian alloys from the royal tombs of Sipán and from Museum of Sicán: non-destructive XRF analysis with a portable equipment”, *Archéo Sciences*, vol. 33, pp. 281-287 (2009).

[3] F.A.C.R.A. Sanches, et al., “Characterization of a sacred statuette replica of “Nossa Senhora da Conceição Aparecida” using X-ray spectrometry techniques”, *Radiation physics and chemistry*, vol.167, 108266 – x (2020).

[4] R.P. Freitas, “Analysis of a Brazilian baroque sculpture using Raman spectroscopy and FT-IR”, *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc*, vol. 154, pp. 67-71 (2016).

[5] L. Bonizzoni et al., “Use of integrated non-invasive analyses for pigment characterization and indirect dating of old restorations on one Egyptian coffin of the XXI dynasty”, *Michrochemical Journal*, vol 138, pp. 122-131 (2018).

[6] R. J. Gettens, H. Kuhn e W. T. Chase, “Identification of the materials of paintings - LEAD WHITE”. vol. 12, pp.125-140 (1967).

[7] “COLOURLEX website”, https://colourlex.com (2021).

[8] W.D. Silva and C.R. Appoloni, “Pigmentos: propriedades físicas, químicas e o período histórico de utilização”. *Publicação Técnica PT* - Laboratório de Física Nuclear Aplicada Depto. de Física – Universidade Estadual de Londrina, Londrina, vol. 13 (2009).